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Evaluation of partially hydrogenated methyl esters of soybean oil as biodiesel*

Biodiesel, an alternative fuel derived from vegetable oils or animal fats, continues to undergo rapid worldwide growth. Specifications mandating biodiesel quality, most notably in Europe (EN 14214) and the USA (ASTM D6751), have emerged that limit feedstock choice in the production of biodiesel fuel. For instance, EN 14214 contains a specification for iodine value (IV; 120 g I_2/100 g maximum) that eliminates soybean oil as a potential feedstock, as it generally has an IV >120. Therefore, partially hydrogenated soybean oil methyl esters (PHSME; IV = 116) were evaluated as biodiesel by measuring a number of fuel properties, such as oxidative stability, low-temperature performance, lubricity, kinematic viscosity, and specific gravity. Compared to soybean oil methyl esters (SME), PHSME were found to have superior oxidative stability, similar specific gravity, but inferior low-temperature performance, kinematic viscosity, and lubricity. The kinematic viscosity and lubricity of PHSME, however, were within the prescribed US and European limits. There is no universal value for low-temperature performance in biodiesel specifications, but PHSME have superior cold flow behavior when compared to other alternative feedstock fuels, such as palm oil, tallow and grease methyl esters. The production of PHSME from refined soybean oil would increase biodiesel production costs by US$ 0.04/L (US$ 0.15/gal) in comparison to SME. In summary, PHSME are within both the European and American standards for all properties measured in this study and deserve consideration as a potential biodiesel fuel.

Keywords: Biodiesel, low-temperature performance, lubricity, oxidative stability, partial hydrogenation.

1 Introduction

Biodiesel (BD), defined as the simple monoalkyl esters of fatty acids derived from transesterified vegetable oils or animal fats, is an attractive alternative to conventional diesel fuel (CDF). Aside from being derived from renewable resources, BD has a number of advantages over CDF, such as reduction of most exhaust emissions [1, 2], improved lubricity [3], higher flash point, improved biodegradability, and reduced toxicity [4]. Furthermore, a number of BD fuel properties are comparable to CDF, such as viscosity, gross heat of combustion and cetane number [1, 2]. However, BD is still faced with technical challenges, such as oxidative stability, low-temperature performance, and nitrogen oxides (NO_x) emissions [4]. In spite of these unresolved issues, BD use in both Europe and the USA has increased dramatically in recent years due to the high price of crude oil and various governmental incentives and mandates for alter-

native fuel use, such as the US Energy Policy Act of 1992 and the European Union (EU) Directive 2003/30/EC.

The feedstock for BD production varies considerably with location according to climate and feedstock availability. Generally, the most abundant lipid in a particular region is the most common feedstock. Thus, rapeseed oil (RSO) and sunflower oil (SFO) are predominantly used in Europe, palm oil (PO) predominates in tropical countries, and soybean oil (SBO) and animal fats in the USA [5]. Accordingly, each region of the world has developed, or is currently developing, BD standards to fit prevailing regional agricultural and political requirements. For instance, the EU standard (EN 14214) is written to include RSO and SFO as feedstocks for BD production, but SBO is disqualified by the inclusion of an iodine value (IV) parameter (EN 14111) of 120 g I_2/100 g maximum (Tab. 1). The American standard, ASTM D6751 [6], has no IV requirement, thereby allowing

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the use of SBO for BD production in the USA. SBO contains a significantly higher quantity of polyunsaturated fatty acids (PUFA; 18:2, 18:3) than either RSO or SFO (Tab. 1), which accounts for its higher IV [7, 8]. Increased levels of PUFA also contribute to the reduced oxidative stability of SBO in comparison to RSO or SFO through accelerated autoxidation at the higher number of allylic and bis-allylic positions on the fatty acid (FA) backbone [9]. The relative rates of autoxidation of the unsaturates given in the literature [9] clearly demonstrate this point: 1 for oleates (18:1), 41 for linoleates (18:2), and 98 for linolenates (18:3).

We set out to evaluate the potential of partially hydrogenated soybean oil (PHSBO) as a feedstock for BD production. With reduced levels of PUFA achieved through catalytic hydrogenation of SBO [7, 10–12], PHSBO should, after transesterification, afford partially hydrogenated soybean methyl esters (PHSME) that both meet the EU BD specification for IV and provide a fuel with improved oxidative stability over soybean oil methyl esters (SME) derived from SBO. Other relevant fuel parameters of interest in this study include low-temperature properties, lubricity, specific gravity, and kinematic viscosity.

2 Materials and methods

2.1 Materials

Nysosel 645 was a gift from the Engelhard Corporation (Iselin, NJ, USA) and is described by the manufacturer as an edible oil hydrogenation catalyst recommended for

partial hydrogenation. It is 15–25% nickel suspended in hardened vegetable oil. Refined SBO was obtained from ADM Oils & Fats (Decatur, IL, USA), and Tonsil bleaching clay from Süd-Chemie (Munich, Germany). All other chemicals and reagents were obtained from Aldrich Chemical Company (Milwaukee, WI, USA) and used as received.

2.2 Synthesis of PHSME and SME from SBO

The hydrogenation of refined SBO was performed in a 2-L Parr Instruments (Moline, IL, USA) model 4561 high-pressure reactor. Temperature and pressure were controlled and monitored using LabVIEW software (National Instruments, Austin, TX, USA). The reactor was charged with approximately 880 g SBO and 0.5 g Nysosel 645 catalyst and heated under vacuum at 170 °C prior to the addition of H_2 up to 100 kPa (1.0 bar). The reaction proceeded under these conditions and was monitored by refractive index (RI) taken at 26 °C. The RI was correlated to IV using a standard curve prepared from samples of known IV, as previously reported [7, 10, 11]. When the target RI was reached, the system was purged with N_2 and H_2 flow was stopped. The cooled oil was treated with 1 mL of a 50% (wt/vol) citric acid solution (to precipitate the nickel catalyst) and 1 g Tonsil bleaching clay. The oil was then filtered through a pad of celite to afford PHSBO. The transesterification of both PHSBO and refined SBO with methanol (6 : 1 molar ratio of alcohol to oil) and NaOH (1 wt-%) was carried out (1 h, 60 °C) as described

Tab. 1. Comparison of typical FA compositions[†] and IV[†] of common BD feedstocks and CP† (°C) and PP[†] (°C) of the corresponding FAME.

Oil: Region:	RSO Europe	SFO[§] Europe	PO Tropical	SBO USA	BT[‡] USA	Grease[#] USA
14:0	tr	tr	tr	tr	3	1
16:0	4	4	44	11	27	17
18:0	2	5	4	4	7	11
16:1	tr	tr	tr	tr	11	2
18:1	56	81	40	22	48	56
18:2	26	8	10	53	2	10
18:3	10	tr	tr	8	tr	2
other	2	2	2	2	2	1
IV	94–120	78–90	50–55	120–143	35–48	N/A[††]
CP of FAME	−3	0	16	0	17	8
PP of FAME	−9	−3	13	−2	15	6

[†] From [7], [8], [5], and [5], respectively.
[‡] Beef tallow
[§] High-oleic
[#] Yellow grease
[††] N/A = not available.

previously [13] to provide PHSME and SME in high yield (96 and 97%, respectively), which were verified by ^{1}H-NMR analysis (Fig. 1).

## 2.3 Composition and quality of PHSME and SME

2.3.1 Fatty acid profile by GC

Fatty acid methyl esters (FAME) in SME and PHSME were separated using a Varian (Walnut Creek, CA, USA) 8400 GC equipped with a flame ionization detector and an SP2380 (Supelco, Bellefonte, PA, USA) column (30 m × 0.25 mm i.d., 0.20 μm film thickness). Carrier gas was He at 1 mL/min. The oven temperature was initially held at 150 °C for 15 min, then increased to 210 °C at 2 °C/min, followed by an increase to 220 °C at 50 °C/min. The injector and detector temperatures were set at 240 and 270 °C, respectively. FAME peaks (Tab. 2) were identified by reference to the retention times of known reference standards.

Tab. 2. FA profiles of SME and PHSME by GC.

Fatty acid	SME	PHSME
14:0	0.1	0.1
16:0	10.6	10.3
18:0	5.3	5.1
20:0	0.5	0.5
22:0	0.4	0.4
18:1	23.3	31.7
18:2	52.6	40.2
18:3	7.2	3.5
18:1 (*Z*)	0	5.9
18:2[†]	0	1.8
total saturates	16.9	16.4
total unsaturates	83.1	83.6
total *trans*-FA	0	7.7
total PUFA	59.8	44.7

† 18:2 (*Z,Z*), (*E,Z*), and (*Z,E*).
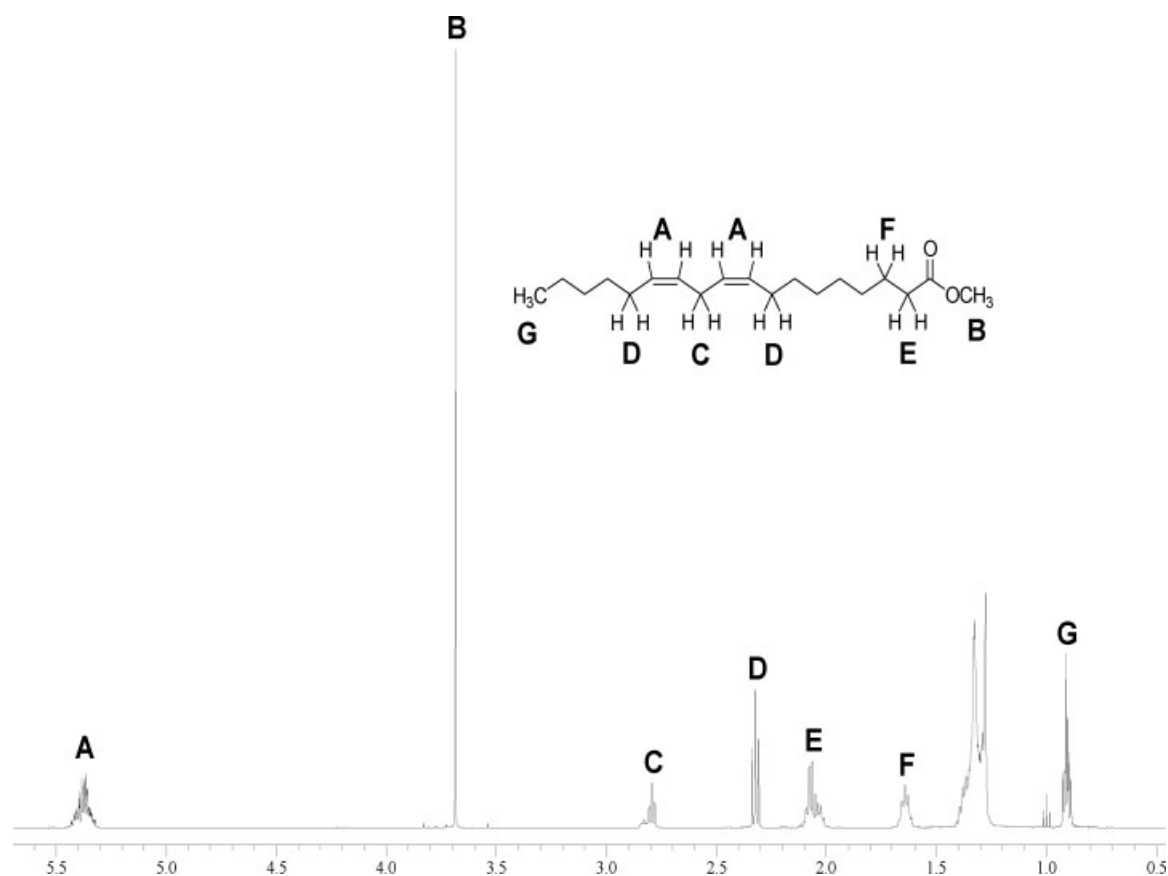
Fig. 1. ^{1}H-NMR spectrum of SME. Methyl linoleate is shown for peak assignment convenience. The small triplet at δ 1 ppm is the terminal methyl group of methyl linolenate and the multiplet at δ 1.3–1.4 ppm corresponds to the numerous methylene protons of the FA backbone. Note: With the notable exception of differing integration values, the ^{1}H-NMR spectrum of PHSME is essentially identical to that of SME.

2.3.2 ^{1}H-NMR verification of PHSME and SME

^{1}H-NMR data of SME and PHSME were recorded using a Bruker AV-500 spectrometer (Billerica, MA, USA) operating at 500 MHz using a 5-mm broadband inverse Z-gradient probe in $CDCl_3$ (Cambridge Isotope Laboratories, Andover, MA, USA) as solvent.

2.3.3 Acid value

Acid value (AV; mg KOH/g sample) titrations were performed as described in AOCS Acid Value Method Cd 3d-63 [14] using a Metrohm 836 Titrando (Westbury, NY, USA) autotitrator equipped with a model 801 stirrer, a Metrohm 6.022 9 100 Solvotrode, and Tiamo 1.1 Light software. However, the official method was modified for scale to use 2 g of sample and 0.02 M KOH. The titration endpoint was determined by the instrument and visually verified using a phenolphthalein indicator. Each sample was run in duplicate and an average value is reported (Tab. 3).

2.3.4 Peroxide value

Peroxide values (PV; meq of peroxide/kg sample) of PHSME and SME were determined prior to further oxidative stability studies using the modified ferric thiocyanate method of Shantha and Decker [15] as described by Hu *et al.* [16]. Hydroperoxides were calculated using a standard

Tab. 3. IV, AV, and PV of SME and PHSME.

	SME	PHSME
IV	124[#]	116[§]
AV[†]	0.31	0.44
PV[‡]	0.83	0.59

[†] Means (*n* = 2), standard deviation (σ) ± 0.05 mg KOH/g.
[‡] Means (*n* = 3), σ ± 0.08 meq/kg.
[§] Determined by method in [10] and [11], σ ± 1 g I_2/100 g.
[#] Provided by manufacturer.

curve made from solutions of ferric chloride (0–15 μg Fe^{3+}). Each sample was run in triplicate and an average value is reported (Tab. 3). PV of less than 1.0 were considered acceptable for further pressurized differential scanning calorimetry (PDSC) and oxidative stability index (OSI) studies.

2.4 Analysis of PHSME and SME

2.4.1 Low-temperature properties

Cloud point (CP) and pour point (PP) determinations were made in agreement with ASTM D5773 [17] and ASTM D5949 [18] using a Phase Technology Analyzer model PSA-70S (Richmond, B.C., Canada). Each sample was run in triplicate and an average value is reported (Tab. 4).

Tab. 4. CP (°C), PP (°C), kinematic viscosity (υ, mm²/s) specific gravity (SG), lubricity (μm), OT (°C), SMT (°C), and OSI value (h) of PHSME and blends thereof (wt-%) in SME.

	0% PHSME	10% PHSME	20% PHSME	50% PHSME	100% PHSME
CP[†]	0	1	1	2	3
PP[†]	−2	−2	−1	−1	0
υ[‡] @ 25 °C	5.8	5.9	6.1	6.7	7.0
υ[‡] @ 40 °C	4.1	4.3	4.4	4.7	5.0
SG[§] @ 25 °C	0.88	0.88	0.88	0.88	0.88
SG[§] @ 40 °C	0.89	0.89	0.89	0.89	0.89
Lubricity[#]	132	151	156	161	180
OT[††]	163	171	173	174	175
SMT[††]	192	193	194	195	205
OSI[‡‡] @ 60 °C	59	61	64	76	160
OSI[§§] @ 110 °C	2.3	2.5	2.8	4.3	6.2

[†]   Means (*n* = 3), σ ± 2 °C.
[‡]   Means (*n* = 3), σ ± 0.2 m2/s.
[§]   Means (*n* = 3), σ ± 0.02.
[#]   Means (*n* = 2), σ ± 4 μm.
[††] Means (*n* = 2), σ ± 1 °C.
[‡‡] Means (*n* = 2), σ ± 3 h.
[§§] Means (*n* = 2), σ ± 0.2 h.

CP and PP are rounded to the nearest whole degree (°C). For a greater degree of accuracy, PP measurements were done with a resolution of 1 °C instead of the specified 3 °C increment.

2.4.2 Lubricity

Lubricity determinations were performed at 60 °C (controlled to less than ±1 °C), according to the standard method ASTM D6079 [19] using a high-frequency reciprocating rig (HFRR) lubricity tester (PCS Instruments, London, UK) *via* Lazar Scientific (Granger, IN, USA). All wear scar (μm) values given here (Tab. 4) are the averages of two replicates, measuring the maximum value of the *x*- and *y*-axis of each wear scar. The average wear scar diameter of each replicate was determined by calculating the average of the *x*- and *y*-axis wear scar lengths.

2.4.3 Rheology

Kinematic viscosity (25, 40 °C) and specific gravity (25, 40 °C) data were determined following ASTM method D7042 [20] using an Anton Paar Stabinger Viscometer model SVM3000 (Ashland, VA, USA). Each sample was run in triplicate and an average value is reported (Tab. 4).

2.4.4 PDSC oxidation method

The experiments were carried out using a DSC 2910 thermal analyzer from TA Instruments (Newcastle, DE, USA). Typically, a 2 μL sample, resulting in a film thickness of <1 mm, was placed in an aluminum pan hermetically sealed with a pinhole lid, and oxidized in the presence of air. Dry air (Gateway Airgas, St. Louis, MO, USA) was pressurized in the module at a constant pressure of 1378.95 kPa (200 psi), and a 10 °C/min heating rate from 50 to 250 °C was used during the experiment. The onset temperature (OT) and signal maximum temperature (SMT) of oxidation were calculated from the exotherm of each curve. Each sample was run in duplicate and average values rounded to the nearest whole degree (°C) are reported (Tab. 4).

2.4.5 OSI oxidation method

The Oil Stability Instrument was manufactured by Omnion (Rockland, MA, USA) under license from Archer Daniels Midland Co. (Decatur, IL, USA). Generally, the procedure given in AOCS OSI method Cd 12b-92 [21] was followed. The apparatus as described in that method was modified slightly by extending the effluent vent by approximately 20–25 cm using an inverted Pasteur pipette placed in the stopper of the sample tube. This minimized evaporative loss of the deionized water used as solvent in the conductance cell. All OSI values given here (Tab. 4) are the average of two replicates. Replications were performed simultaneously on the OSI instrument.

3 Results and discussion

3.1 Composition of PHSME and SME

The synthesis of PHSME and SME was accomplished using previously described methods [7, 10–12] and each was analyzed for quality (^{1}H-NMR; Fig. 1) and FA composition (GC; Tab. 2). It is known that partial hydrogenation of unsaturated vegetable oils results not only in simple reduction, but also double bond migration and isomerization of *cis* double bonds into the thermodynamically more stable *trans* configuration [7]. As seen in Tab. 2, SME have a typical FA composition (see Tab. 1 for comparison) by GC analysis and, as expected, PHSME contain some *trans*-FA constituents (7.7%). The total amount of PUFA (44.7%) also is reduced in comparison to SME (59.8%), another expected result. In fact, the amount of methyl linolenate (18:3), the FAME most susceptible to autoxidation, has been cut in half from SME (7.2%) to PHSME (3.5%). However, the overall amount of saturates *vs.* unsaturates is essentially unchanged from SME to PHSME because the amount of monounsaturates has increased from SME (23.3%, 18:1) to PHSME (37.6%, 18:1 + 18:1 (*Z*)).

Both SME and PHSME were evaluated for AV, PV and IV (Tab. 3). Both ASTM D6751 and EN 14214 specify a maximum allowable AV in BD of 0.50 mg KOH/g, and both PHSME and SME are within acceptable limits (Tab. 3). PV determinations were particularly important, since initially low levels of autoxidation are preferred when conducting oxidation stability studies for reliable results [9]. Therefore, PV <1 was considered acceptable for further study and both PHSME and SME were within this limit (Tab. 3). Since EN 14214 mandates a maximum allowable IV of 120, SBO (IV = 124) was subjected to partial hydrogenation to an IV of 116. Lower IV were not desirable in this study because of their potential impact on other fuel properties, most notably low-temperature performance.

3.2 Low-temperature properties

It is known that high levels of saturated and *trans*-FAME in BD fuel have a deleterious effect on the low-temperature operability of that BD [5, 7, 22–24]. Such FAME crystallize

at higher temperatures than their *cis*-unsaturated counterparts and, as a result, may plug engine filters and fuel lines during winter months in temperate climates [23]. Not surprisingly, PHSME, which contain a significant amount of methyl *Z*-9-octadecenoate and other *trans*-FAME (Tab. 2), fall into this class of BD fuels (Tab. 4). The CP and PP observed for PHSME (100%: CP 3 °C, PP 0 °C; Tab. 4), however, are not as high as those observed for methyl tallowate (CP 17 °C, PP 15 °C) [25], methyl palmate (CP 15 °C, PP 13 °C) [5], or yellow grease methyl esters (CP 8 °C, PP 6 °C) [26], all of which have elevated levels of saturated FA in comparison to the common feedstock oils (Tab. 1). In fact, the difference between PHSME and SME (CP 0 °C, PP −2 °C; Tab. 1) is only 3 °C (CP) and 2 °C (PP), which is remarkable considering the *trans* content of PHSME in comparison to SME. As expected, a corresponding increase in CP and PP was observed as the blend level (wt-%) of PHSME in SME was gradually increased from 0 to 100% (Tab. 4). Rapeseed methyl esters (RME) have superior cold weather operability (CP –3 °C, PP –9 °C; Tab. 1) when compared to both SME and PHSME.

3.3 Lubricity and viscosity

Although both ASTM D6751 and EN 14214 do not currently contain lubricity specifications, it is nonetheless a critical fuel property. Fuels with poor lubricity can cause failure of diesel engine parts that rely on lubrication by the fuel, such as fuel pumps and injectors [5, 27]. As such, lubricity specifications are included in petrodiesel standards in the USA (ASTM D975) and EU (EN 590). The specified maximum allowable wear scars are 460 μm (at 60 °C) in EN 590 [28] and 520 μm (at 60 °C) in ASTM D975 [29]. However, a recent study indicated that fuels with wear scars greater than 460 μm (at 60 °C) may not possess sufficient lubricity for practical use in a diesel engine [30]. Both the SME and PHSME lubricity data reported here (Tab. 4) at 60 °C are significantly lower than the prescribed lubricity in either standard, indicating that either material would be acceptable with regard to lubricity. However, an increase in the average wear scar size was noticed as the percentage of PHSME in SME was increased from 0 to 100% (Tab. 4). A reduction in the total number of double bonds, indicated by a reduction in PUFA in PHSME in comparison to SME (Tab. 2), may explain this result, as it is known that increasing unsaturation imparts more favorable lubricity on a substance [5]. Other studies [27] have demonstrated that the double bond configuration does not play a significant role in lubricity; therefore the increase in the *trans* content of PHSME is not a likely cause for the reduction in lubricity of PHSME.

Kinematic viscosity limits are specified both in ASTM D6751 (1.9–6.0 mm^2/s at 40 °C) and EN 14214 (3.5–5.0 mm^2/s at 40 °C) for BD fuels. Viscosity is an important fuel property because it affects the atomization of a fuel upon injection into the diesel engine combustion chamber and, ultimately, the formation of engine deposits [5]. Fuels with higher viscosities are more likely to cause such problems. In fact, high viscosity is the major fuel property explaining why neat vegetable oils have been largely abandoned as alternatives to CDF. In the current study, both PHSME and SME have kinematic viscosities (Tab. 4) that fall within both the American and EU BD specification ranges. However, an increase in kinematic viscosity was noticed as the percentage of PHSME in SME increased from 0 to 100% (Tab. 4), indicating that the increase in *trans* content of the fuel results in a corresponding increase in viscosity, which is in agreement with earlier studies [5, 31]. The specific gravity (SG) of PHSME and SME (Tab. 4) was nearly identical and was unaffected by either temperature or blend level of PHSME in SME.

3.4 Oxidative stability by PDSC and OSI

Catalytic partial hydrogenation is known to increase the oxidative stability of a substance [7, 9]. As expected, PHSME showed improved oxidative stability over SME, as determined by both PDSC and OSI analysis (Tab. 4). The SMT (°C), measured by PDSC, increased significantly as the blend level of PHSME in SME increased from 0 to 100%, indicating an increase in oxidative stability. The reduction in PUFA (Tab. 2) from SME to PHSME, as mentioned previously, explains this result. The OT (°C) also increased significantly as the blend level increased to 20%, but did not increase significantly from 20 to 100% PHSME in SME (Tab. 4).

The determination of oxidative stability by the OSI, as specified by AOCS OSI method Cd 12b-92 [21], is equivalent to the European Rancimat test and is generally done at a temperature of 110 °C. However, other researchers [32–34] have reported that an OSI block temperature (T_B) of 110 °C is not suitable for evaluating high-IV BD such as SME, due to rapid oxidative degradation, and a more appropriate T_B = 60 °C was recommended. Therefore OSI values at both T_B = 60 and 110 °C are reported in Tab. 4. Although an OSI time of 160 h was obtained for PHSME at T_B = 60 °C, which is significantly better than that for SME (59 h), it should be noted that previous studies [35, 36] terminated OSI experiments at 90 h because it was shown that variances in OSI values tended to increase with increasing OSI value. At both T_B = 60 and 110 °C, a significant increase in OSI time was

noticed as the blend level of PHSME in SME was increased from 0 to 100%. However, EN 14214 specifies an oxidation stability (at 110 °C) time of at least 6 h by the Rancimat method (EN 142112). Neat PHSME was the only sample to meet this requirement (OSI: 6.2 h), as can be seen in Tab. 4.

3.5 Cost analysis

About 80–85% of the overall cost of BD is associated with feedstock cost, so it is of paramount importance when considering BD economics. The remaining costs include chemicals, energy, labor, depreciation, overhead, administration, and maintenance [37, 38]. For a plant producing about 37,800,000 L per annum (10,000,000 gal) of BD fuel, the feedstock (refined SBO) cost is US$ 0.43/L (US$ 1.61/gal). All other expenses account for US$ 0.10/L (US$ 0.38/gal). Thus, the total cost of BD production is US$ 0.53/L (US$ 1.99/gal) [39]. Any additional modifications to the feedstock, such as partial hydrogenation, will naturally add to the overall cost of BD production. The increased costs associated with catalyst, hydrogen, and operating expenses to produce PHSBO from SBO will add US$ 0.04/L (US$ 0.15/gal) to the overall cost of BD production [38, 40], which will result in an increase in BD production expenses from US$ 0.53/L (US$ 1.99/gal) to US$ 0.57/L (US$ 2.14/gal). Increased costs of BD production from PHSBO may be mitigated by the high price of crude oil, which may allow BD from PHSBO to remain cost-competitive with CDF.

4 Conclusions

Compared to SME, PHSME were found to have better oxidative stability, similar specific gravity, but inferior low-temperature properties, kinematic viscosity, and lubricity. However, both kinematic viscosity and lubricity of PHSME were within the prescribed US and EU limits. There is no universal value for low-temperature performance in either EN 14214 or ASTM D6751, but PHSME have better cold flow properties when compared to other alternative feedstock fuels, such as palm oil, tallow and grease methyl esters. In summary, PHSME are within both the European and American standards for all properties measured in this study and deserve consideration as a potential BD fuel. Furthermore, previous studies [41] show that NOx emissions increase with increasing unsaturation. Therefore, a reduction in the level of PUFA may provide a fuel with improved NOx emissions over that of SME. As such, a promising area of future study may include exhaust emission testing and cetane number determination of PHSME in comparison to SME.

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